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Aluminium complexes of B- and N-based hydrides: Synthesis, structures and hydrogen storage properties☆

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ABSTRACT

The storage of hydrogen in a solid state is one of the main challenges for stationary and mobile applications. Light metal hydrides have attracted significant attention as potential candidates for energy storage. Remarkably, Al-containing hydrides, namely AlH_3 and $M(AlH_4)_n$, are among the most fascinating classes of materials, able to cycle up to 5.5 wt% of hydrogen at moderate temperatures. This review covers the recent research on the families of Al-based complex hydrides involving other light elements such as B and N. They were classified according to the charge of the Al-based complexes, as anionic, molecular, cationic or "autoionized" where Al is centering both the cation and the anion. The factors influencing the stability and the hydrogen purity of the series of anionic aluminium amides $M[Al(NH_2)_4]_n$, borohydrides $M[Al(BH_4)_4]$ and amidoboranes $M[Al(NH_2BH_3)_4]$, as well as molecular $[Al(L)(BH_4)_3]$ (L = molecular ligands) and cation $[Al(NH_3)_6]^{3+}$-based complexes are discussed. In particular, the ability of the strong Lewis acid Al^{3+} to coordinate both the initial hydrogenated species as well as their dehydrogenation products makes it a good template for chemical transformations involving light chemical and complex hydrides.

Introduction

An increase in the consumption of non-renewable fossil fuels is producing not only a challenge of new sustainable energy carriers, but also leads to environmental pollution and climate changes induced by carbon dioxide CO_2. Thus the transition towards a new carbon-free and reliable energy system capable of substituting current and future energy demands is one of the greatest challenges of the 21st century. In line with these demands, hydrogen has an extreme potential as the cleanest energy carrier, see e.g. Ref. [1]. It can be produced from renewable energy sources by electrolytic water splitting from hybrid solar–hydrogen or other systems [2]. However, a major challenge in the future of the "hydrogen economy" is the development of efficient hydrogen storage systems, especially for mobile applications [3,4]. In particular, the efficient storage of pressurized and liquefied hydrogen has technical issues of high pressures (350–700 bar) and cryogenic temperatures (−253 °C) [4]. That is why in recent years much attention was paid to solid state hydrogen storage in a form of light metal complex and chemical hydrides, from which hydrogen can be released either by thermolysis or via hydrolysis [5–8].

☆ Dedicated to the 65 years anniversary of Professor Gérald Pourcelly.

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Mobile applications is one of the most important directions for the "hydrogen economy". According to the U.S. Department of energy, perspective systems for mobile applications require high hydrogen content which should be above 5.5 wt %, and a low gravimetric density of 40 g/L [9]. The second important detail is a low operational temperature (60–120 °C), suitable for proton-exchange membrane fuel cells PEMFC [10]. These requirements, together with reversibility, are limiting the number of possible solid state hydrogen storage systems. It is noteworthy that nowadays most of the advanced systems in terms of these limitations should contain light atoms (approximately with atomic number $Z \leq 13$). That is why Al-containing hydrides of AlH_3 [11,12] and alkali metal alanates of $M[AlH_4]_n$ [e.g. 13], which potentially contain up to 10.1 wt% of hydrogen and a metal which is highly abundant in nature, has attracted a great deal of attention. $NaAlH_4$ is the most intensively studied member of Al-based hydrides due to its high hydrogen capacity of 5.6 wt% and hydrogen release reversibility, when catalyzed by a small amount of a transition metal catalyst (e.g. 2–4 mol% Ti) [14–16]. This fascinating discovery was a breakthrough in solid state hydrogen storage since it exhibits approximately twice the reversible capacity of any of the conventional metal hydrides (e.g. $LaNi_5H_x$, $FeTi_2H_x$) [17]. Since that time, the systems of AlH_3 and $M[AlH_4]_n$ have been intensively investigated both in terms of their crystal structures [18] and hydrogen storage properties [13].

The interest in Al-containing complex hydrides and their reactive hydride composites (RHC) as perspective hydrogen storage systems remained high during last two decades. Indeed, in recent years, many new Al-based complex hydrides involving other light elements such as N and B have been characterized. In particular, the synthesis, crystal structures, thermal decomposition and hydrogen storage properties of hydridic $M[Al(NH_2)_4]_n$ ($M = Li^+, Na^+, K^+, Rb^+, Cs^+$, $n = 1$; $M = Ca^{2+}, Mg^{2+}, Sr^{2+}, Ba^{2+}$) [19,20] and $M[Al(BH_4)_4]$ ($M = Li^+, Na^+, K^+, NH_4^+, Rb^+, Cs^+$) have been presented recently [21,22]. The other direction of perspective B,N-containing systems is making use of $N{-}H^{\delta+}\cdots H^{\delta-}{-}B$ dihydrogen bonds, which play an important role in molecular packing in crystals and in H_2 evolution [23]. In line with this criteria, several Al-based B- and N-containing hydrides, such as an anionic $Na[Al(NH_2BH_3)_4]$ [24], molecular $[Al(NH_3BH_3)(BH_4)_3]$ [25] and cation $[Al(NH_3)_6]^{3+}$ derivatives, namely $[Al(NH_3)_6][BH_4]_3$ [26], $[Al(NH_3)_6][Li_2(BH_4)_5]$ and $[Al(NH_3)_6][Li_2(BH_4)_5]\cdot 3NH_3BH_3$ have been investigated [27,28].

This review paper will give a short description of synthesis, crystal structure and hydrogen storage properties of aluminium complexes with B- and N-based hydrides. We will not cover the systems where only hydrogen atoms are surrounding the central Al atom, such as alanates and in alane, referring the reader to the existing recent reviews [11–13]. Here we focus on those compounds where Al^{3+} cation is coordinating to complex hydrides created by other light elements such as B and N. Borohydrides $M(BH_4)_n$, amides $M(NH_2)_n$ and amidoboranes $M(NH_2BH_3)_n$ themselves carry a significant amount of hydrogen, but their chemistry with alkali and alkali-earth metals is limited by the choice of metals [29–31]. Introducing another complex-forming elements allows tuning stability of bimetallic series, as illustrated for example by Zn- and Cd-based borohydrides [32,33]. Importantly, the complex-forming metal, possessing higher electronegativity, is determining the stability of the bimetallic hydride [34]. Aluminium stands in the bimetallic series on its own, given its high polarizing power defined by the exceptional charge-to-radius ratio, low weight, high natural abundance, and the fact that the chemistry of Al complexes with B- and N-based hydrides has been explored only recently. Being an excellent Lewis acid, Al^{3+} is capable of coordinating the initial B- and N-based complex hydrides and their dehydrogenation products, thus serving as a template (or a matrix) for potential reversible dehydrogenation. The activation of neutral molecules, namely ammonia and ammonia borane, also requires a highly polarizing cation and have attracted increasing interest [7].

The systems listed above will be divided into three main groups. The first contains Al-centered complex anions, namely $M[Al(NH_2)_4]_n$, $M[Al(BH_4)_4]$ and $M[Al(NH_2BH_3)_4]$. The second are the molecular complexes and the third are complexes containing Al within complex cations, as for example $[Al(NH_3)_6]^{3+}$. There are also recent examples of "autoionized" complexes, where Al forms complex cation and anion within the same compound. The presence of dihydrogen bonds will be considered along with the cation Al–N and Al–B complex hydrides.

Synthesis

Synthesis of anionic $M[Al(NH_2)_4]_n$ ($M = Li^+, Na^+, K^+, Rb^+, Cs^+$, $n = 1$; $M = Ca^{2+}, Mg^{2+}, Sr^{2+}, Ba^{2+}$, $n = 2$)

The synthesis of $M[Al(NH_2)_4]_n$ can be performed in different ways, using the metals or their hydrides in presence of NH_3. Most of the alkali metal aluminium amides can be obtained by the reaction of Al in solution of the metals in liquid NH_3 [35]:

$$M + Al + 4NH_3 \rightarrow M[Al(NH_2)_4] + 2H_2 \ (M = \text{alkali metal}) \quad (1)$$

$M[Al(NH_2)_4]$ can be also formed from the reaction of the corresponding $MAlH_4$ with NH_3 [36]:

$$MAlH_4 + 4NH_3 \rightarrow M[Al(NH_2)_4] + 4H_2 \ (M = \text{alkali metal}) \quad (2)$$

The formation of $M[Al(NH_2)_4]_n$ (M = alkali or alkali earth metal) is also observed in the mechanochemical reaction of alkali and alkali earth metal hydrides with Al under NH_3 gas [19,20]:

$$MH_n + nAl + 4nNH_3 \rightarrow M[Al(NH_2)_4]_n + 2.5nH_2 \quad (3)$$

The mechanochemical treatment of their hydrides under liquid NH_3 yields $M[Al(NH_2)_4]_n$ (M = alkali or alkali earth metal):

$$MH_n + nAlH_3 + 4nNH_3 \rightarrow M[Al(NH_2)_4]_n + 4nH_2 \quad (4)$$

$Ba[Al(NH_2)_4]_2$ is found to be quite unstable at ambient conditions without ammonia pressure [37]. Recently, low temperature a single crystal measurement has revealed the crystal structure of $Ba[Al(NH_2)_4]_2 \cdot 2NH_3$, which was synthesized in ammonothermal conditions from an intermetallic phase with Al_2Ba composition [38]. A similar ammoniate of $Ca[Al(NH_2)_4]_2 \cdot NH_3$ composition was also reported [39].

Synthesis of anionic $M[Al(BH_4)_4]$ ($M = Li^+$, Na^+, K^+, NH_4^+, Rb^+, Cs^+) complexes

$Al(BH_4)_3$ has a high potential for hydrogen and energy storage, due to its high hydrogen content of 16.9 wt%. However, this is a highly pyrophoric liquid at ambient conditions, explosive in contact with air, and thus dangerous for practical applications. This feature is used in jet engines as an ignition source and has also been examined for possible application as a rocket fuel [40]. Thus, the stabilization of $Al(BH_4)_3$ in form of more stable complexes is one of the challenges for hydrogen and energy storage.

One of the first attempts to stabilize $Al(BH_4)_3$ with another alkali-metal borohydrides was performed by a reaction of MBH_4 and $Al(BH_4)_3$, which yields $M[Al(BH_4)_4]$ ($M = Li^+$ and K^+) [41,42]. Similar synthesis of the whole family of $M[Al(BH_4)_4]$ ($M = Li^+$, Na^+, K^+, NH_4^+, Rb^+, Cs^+) was performed recently by the interaction of $Al(BH_4)_3$ with alkali metal borohydrides [21,22,43]:

$$MBH_4 + Al(BH_4)_3 \rightarrow M[Al(BH_4)_4] \ (M = Li^+, Na^+, K^+, NH_4^+, Rb^+, Cs^+) \quad (5)$$

Remarkably, $LiBH_4$ forms two different mixed-metal borohydrides with $Al(BH_4)_3$. The second representative is $[Li_4(BH_4)][Al(BH_4)_4]_3$, which can be obtained as the first of two stages of the reaction (5):

$$4LiBH_4 + 3Al(BH_4)_3 \rightarrow [Li_4(BH_4)][Al(BH_4)_4]_3 \quad (6)$$

$$[Li_4(BH_4)][Al(BH_4)_4]_3 + Al(BH_4)_3 \rightarrow 4Li[Al(BH_4)_4] \quad (7)$$

The formation of $[Ca(BH_4)][Al(BH_4)_4]$ complex was also claimed [44], but no further structural evidence of alkali-earth aluminium borohydrides formation was reported in the literature.

The mechanochemical synthesis of $M[Al(BH_4)_4]$ ($M = Li^+$, Na^+, K^+) is also known [45,46]. The reported reactions between MBH_4 ($M = Li^+$, Na^+) and $AlCl_3$ revealed Cl-stabilization of $[Li_4(BH_4)][Al(BH_4)_4]_3$ (with composition of $Li_4Al_3(BH_4)_{12.74}Cl_{0.26}$) and formation of $Na[Al(BH_4)_{4-x}Cl_x]$ solid solution having crystal structure different from Cl-free $Na[Al(BH_4)_4]$. The mixture of MBH_4 ($M = Li^+$, K^+) and $AlCl_3$ yields a mixed-metal $LiK(BH_4)_2$ at room temperature [21]. This method has another serious disadvantage of so-called “dead mass” formation of MCl, which significantly reduces the hydrogen storage capacity of the system:

$$3LiBH_4 + 13AlCl_3 \rightarrow [Li_4(BH_4)][Al(BH_4)_4]_3 + 9LiCl \quad (8)$$

$$4NaBH_4 + AlCl_3 \rightarrow Na[Al(BH_4)_{4-x}Cl_x] + 3Na(BH_4)_xCl_{1-x} \quad (9)$$

$$9LiBH_4 + 3KBH_4 + 2AlCl_3 \rightarrow 2K[Al(BH_4)_4] + 6LiCl + LiK(BH_4)_2 \quad (10)$$

Synthesis of anionic $M[Al(NH_2BH_3)_4]$ ($M = Li^+$, Na^+) complexes

The existence of $Al(NH_2BH_3)_3$ was reported by Hawthorne et al. [47], however no structural data is available for this compound to the date. Recently, attention has been paid to bimetallic derivatives $M[Al(NH_2BH_3)_4]$ ($M = Li^+$, Na^+), which can be obtained from the reaction of alanates and ammonia borane (AB) in THF [24,47]:

$$MAlH_4 + 4NH_3BH_3 \rightarrow M[Al(NH_2BH_3)_4] + 4H_2 \ (M = Li^+, Na^+) \quad (11)$$

The formation of $Na[Al(NH_2BH_3)_4]$ in reaction (11) can be also made in solvent-free conditions using mechanochemical synthesis [24]. Remarkably, the reaction of $LiAlH_4$ and AB under ball-milling conditions is violent resulting in amorphous products and metallic aluminium [24,48]. The reaction of Li_3AlH_6 with AB was assumed to yield a composition $Li_3AlH_2(NH_2BH_3)_4$, however this conclusion is not yet confirmed by crystal structure data [48].

Synthesis of molecular and cation Al–N and Al–B complex hydrides

The second way to stabilize $Al(BH_4)_3$ can be performed via coordination of Al to other molecular hydrides, the latter behaving as Lewis bases [49]. In contrast to $M[Al(BH_4)_4]$ ($M = Li^+$, Na^+, K^+, NH_4^+, Rb^+, Cs^+), where Al adopts complex $[Al(BH_4)_4]^-$ anion, the addition of molecules to $Al(BH_4)_3$ can afford Al atoms to form either molecular or cation complexes. In particular, the reaction of $Al(BH_4)_3$ with one equivalent of NH_3, NH_3BH_3 or $CH_3NH_2BH_3$ gives molecular complexes [22,25,50]:

$$Al(BH_4)_3 + L \rightarrow [Al(L)(BH_4)_3] \ (L = NH_3 \text{ or } RNH_2BH_3) \quad (12)$$

Interestingly, in contrast to the reaction (12), an interaction of $CH_3NH_2BH_3$ with $AlCl_3$, results in an autoionized $[Al(CH_3NH_2BH_3)_2Cl_2][AlCl_4]$ complex [22].

The complexes of $Al(BH_4)_3$ with ethylenediamine have also been reported recently [51]. Various compositions of $Al(BH_4)_3 \cdot nC_2H_8N_2$ were proposed according to the addition reactions:

$$Al(BH_4)_3 + nC_2H_8N_2 \rightarrow Al(BH_4)_3 \cdot nC_2H_8N_2, \text{ integer } n < 6 \quad (13)$$

$$Al(BH_4)_3 + Al(BH_4)_3 \cdot nC_2H_8N_2 \rightarrow Al(BH_4)_3 \cdot mC_2H_8N_2, \ m < n \quad (14)$$

The structure of these adducts are not known, except for $n = 4$ [52], however the nature of $Al(BH_4)_3 \cdot nC_2H_8N_2$ is supposed to be ionic. The ligand may be chelating and/or bridging depending on the stoichiometry, like in $C_2H_8N_2$ complexes with $Mg(BH_4)_2$ [53]. A complex with low ligand-to-metal ratio, $Al(BH_4)_3 \cdot nC_2H_8N_2$ ($n = 1/2$), was observed in our most recent work [22], where $C_2H_8N_2$ was generated in low concentrations upon the decomposition of its borane complex:

$$2Al(BH_4)_3 + (CH_2NH_2BH_3)_2 \rightarrow [Al(CH_2NH_2)_2(BH_4)_2][Al(BH_4)_4] + B_2H_6 \quad (15)$$

Numerous molecular dimer complexes can be obtained from ammine boranes and chlorides with AlX_3 as well as $HAlX_2$ ($X = Cl^-$ or BH_4^-). Those containing bulky organic ligands, as e.g. in Ref. [54], will be omitted in this review. On the other hand, an example of such reactions yielding molecular dimers can be shown by the reaction of triethylenediamine (TEDA) mono-borane with $Al(BH_4)_3$ in toluene solution. The latter yields a dimer solvate complex $[HAl(BH_4)_2 \cdot (TEDA)BH_3]_2(PhMe)_2$ [55]. The other dimers, $[H(X)AlNEt_2]_2$ and $[(X)_2AlNEt_2]_2$, were obtained recently by the following reactions [56]:

$$2AlCl_3 + 2LiNEt_2 \rightarrow [Cl_2AlNEt_2]_2 + 2LiCl \quad (16)$$

$$[Cl_2AlNEt_2]_2 + 4LiBH_4 \rightarrow [(BH_4)_2AlNEt_2]_2 + 4LiCl \quad (17)$$

$$2HAlOEt_2 + 2LiNEt_2 \rightarrow [H(Cl)AlNEt_2]_2 + 2LiCl \quad (18)$$

$$[H(Cl)AlNEt_2]_2 + 2LiBH_4 \rightarrow [H(BH_4)AlNEt_2]_2 + 2LiCl \quad (19)$$

The formation of stable chelate complexes is not the only way to stabilize $Al(BH_4)_3$ in a cationic form. In contrast to the reaction (12), an excess of NH_3 over $Al(BH_4)_3$ yields $Al(BH_4)_3 \cdot 6NH_3$, which on the basis of its crystal structure can be written as $[Al(NH_3)_6][BH_4]_3$ [26]:

$$Al(BH_4)_3 + 6NH_3 \rightarrow [Al(NH_3)_6][BH_4]_3 \quad (20)$$

Interestingly, the stable $[Al(NH_3)_6][BH_4]_3$ can be obtained in safe conditions: it forms during the electrolysis of alkali metal borohydrides in liquid NH_3, where Al is used as a dissolving anode [57]:

$$3NaBH_4 + Al + 6NH_3 \rightarrow [Al(NH_3)_6][BH_4]_3 + 3Na \quad (21)$$

Similarly to the reaction (14), a series of $Al(BH_4)_3$ ammoniates can be obtained by mixing the borohydride with $[Al(NH_3)_6][BH_4]_3$ [58]:

$$nAl(BH_4)_3 + [Al(NH_3)_6][BH_4]_3 \rightarrow (n+1)[Al(NH_3)_{(6/(n+1))}(BH_4)_3] \quad (22)$$

The cationic form of $[Al(NH_3)_6]^{3+}$ is stable: the mechanochemical reaction of $[Al(NH_3)_6][BH_4]_3$ with $LiBH_4$ gives a bimetallic complex possessing the same complex cation [27]:

$$[Al(NH_3)_6][BH_4]_3 + 2LiBH_4 \rightarrow [Al(NH_3)_6][Li_2(BH_4)_5] \quad (23)$$

The interaction of other $M(BH_4)_n$ ($M = Na^+$, $n = 1$; $M = Ca^{2+}$ and Mg^{2+}, $n = 2$) with $[Al(NH_3)_6][BH_4]_3$ gives poorly crystalline products with unknown composition [59].

Remarkably, $[Al(NH_3)_6][Li_2(BH_4)_5]$ is also quite reactive with other molecules. In particular, it forms a complex with ammonia borane, $[Al(NH_3)_6][Li_2(BH_4)_5] \cdot 3NH_3BH_3$, in the mechanochemical reaction [28]:

$$[Al(NH_3)_6][Li_2(BH_4)_5] + 3NH_3BH_3 \rightarrow [Al(NH_3)_6][Li_2(BH_4)_5] \cdot 3NH_3BH_3 \quad (24)$$

The first example of aluminium amidoborane ammoniate with suggested composition $[Al(NH_3)_6][Al(NH_2BH_3)_6]$ was published recently [60]. The reported composition and the molecular structure were based on MAS ^{27}Al NMR spectroscopy data. This complex was obtained from a solution of $NH_3BH_3 \cdot nNH_3$ ($n = 1$–6) and $AlH_3 \cdot OEt_2$:

$$2AlH_3 \cdot OEt_2 + 6NH_3BH_3 \cdot nNH_3 \rightarrow [Al(NH_3)_6][Al(NH_2BH_3)_6] + 6(n-1)NH_3 + 2OEt_2 + 6H_2 \quad (25)$$

Crystal structures of Al–B and Al–N complex hydrides

Crystal structures of hydrides with Al–B and Al–N complex anions

Four types of aluminium complex hydrides are known to date: alanates AlH_4^- and AlH_6^{3-}, aluminium amides $[Al(NH_2)_4]^-$, borohydrides $[Al(BH_4)_4]^-$ and amidoboranes $[Al(NH_2BH_3)_4]^-$. The details of their crystal structures are given in Table 1 and the representation of metal cation coordinations is shown in Fig. 1.

In general, complex aluminium amides are analogous to metal alanates, where all atoms of hydrogen in the AlH_4^- tetrahedra are substituted by NH_2^-, forming the complex anion $[Al(NH_2)_4]^-$. Metal cations can be linked to $[Al(NH_2)_4]^-$ by nitrogen atoms via corners or edges of the complex anion. The coordination numbers of M^+ cations in $M[Al(NH_2)_4]_n$ decreases, compared to the corresponding $MAlH_4$, from 5 to 4 for Li^+; from 8 to 4 for Na^+; from 10 to 8 and 6 for α- and β-K $[Al(NH_2)_4]$, respectively; from 8 to 7 for Ca^{2+}. The analysis of the M–N interatomic distances reveals their linear correlation, with an effective ionic radii of the metal similar to the M–H distances in alanates [18].

Borohydrides containing complex anions $[M^{m+}(BH_4)_n]^{(m-n)-}$ are generally constructed by the packing of counter-cations (or complex cations) and complex anions in close-packed inorganic structure types well known amongst the AMO_4 (A = alkali metal) oxide family [61]. However, the mixed-metal $[Li_4(BH_4)][Al(BH_4)_4]_3$ has a unique crystal structure with respect to the $M[Al(BH_4)_4]$ series. The complex cation $[Li_4(BH_4)]^{3+}$ and anion $[Al(BH_4)_4]^-$ are packed similar to the Frank-Kasper Cr_3Si-type phase, see Fig. 1. A topological analysis indicates that $[Li_4(BH_4)][Al(BH_4)_4]_3$ is an antitype of Ag_3PO_4

Table 1 – Crystal structure data for hydrides with Al–B and Al–N complex anions.

Compound	Space group	Cell parameters, Å			α, β, γ (°)	V/Å³	Z	Refs.
		a	*b*	c				
$M[Al(NH_2)_4]_n$								
$Li[Al(NH_2)_4]$	$P2_1/n$	9.478(1)	7.351(1)	7.398(1)	90.26(1)	519.39	4	[67]
$Li[Al(ND_2)_4]$	$P2_1/n$	9.5075(3)	7.3610(2)	7.4076(2)	90.165(3)		4	[20]
$Na[Al(NH_2)_4]$	$P2_1/c$	7.328(2)	6.047(2)	13.151(3)	94.04(1)	581.3	4	[68]
$Na[Al(ND_2)_4]$	$P2_1/c$	7.3317(9)	6.0447(8)	13.151(2)	94.110(9)		4	[20]
$Na_2Al(NH_2)_5$	*Cmma* or *Abm*2	23.56	19.36	6.78		3092.5	16	[69]
α-$K[Al(NH_2)_4]$	$C222_1$	10.00(1)	5.80(1)	10.14(1)		588.12	4	[70]
α-$K[Al(ND_2)_4]$	$C222_1$	10.17258(7)	5.78762(5)	9.98651(7)			4	[20]
β-$K[Al(NH_2)_4]$	*Pnma*	11.37(1)	8.85(1)	6.146(6)		618.44	4	[35]
β-$K[Al(ND_2)_4]$	*Pnma*	11.4183(4)	8.8588(2)	6.1696(2)			4	[20]
$Rb[Al(NH_2)_4]$	*P*4/*n*	7.406(4)	7.406(4)	5.386(4)		295.42	2	[71]
$Cs[Al(NH_2)_4]$	*P*4/*n*	7.563(3)	7.563(3)	5.354(1)		306.24	2	[71]
$Mg[Al(NH_2)_4]_2$	Hex. n/a	12.1	12.1	7.95		1008.02	n/a	[19]
$Ca[Al(ND_2)_4]_2$	*Pc*	6.4321(2)	6.4377(2)	12.2939(3)	90.612(2)		2	[20]
$CaAl(NH_2)_5$	$P4_222$	6.471(5)	6.471(5)	12.244(9)		512.70	4	[72]
$Sr[Al(NH_2)_4]_2$	$P6_2$, $P6_4$, $P6_222$ or $P6_422$	17.49(1)	17.49(1)	28.17(2)		7462.72	36	[37]
$M[Al(BH_4)_4]$								
$Li[Al(BH_4)_4]$	$P2_1/c$	19.6259(4)	13.5317(3)	13.5206(3)	107.457(2)	3425.29(13)	16	[22]
$[Li_4(BH_4)][Al(BH_4)_4]_3$	*P*−43*n*	11.4622(1)	11.4622(1)	11.4622(1)		1505.91(3)	2	[22]
$Na[Al(BH_4)_4]$	*C*2/*c*	9.3375(3)	11.2499(4)	8.4112(3)	104.706(2)	854.61(5)	4	[22]
$Na[Al(BH_4)_2Cl_2]$	$Pmn2_1$	7.9001(4)	7.0033(3)	6.4888(3)		359.0(3)	2	[46]
$K[Al(BH_4)_4]$	*Fddd*	9.7405(3)	12.4500(4)	14.6975(4)		1782.4(3)	8	[21]
	*Fdd*2	9.7407(11)	12.4039(14)	14.6745(20)		1773.0(4)	8	[43]
$NH_4[Al(BH_4)_4]$	*Fddd*	9.8873(4)	12.6005(5)	14.9656(5)		1864.49(13)	8	[22]
$Rb[Al(BH_4)_4]$	*Fddd*	9.8889(4)	13.3009(7)	14.3252(8)		1876.69(7)	8	[22]
ht-$Cs[Al(BH_4)_4]$	$I4_1/amd$	7.8594(3)	7.8594(3)	16.3173(8)		1007.9(1)	4	[22]
$M[Al(NH_2BH_3)_4]$								
$Na[Al(NH_2BH_3)_4]$	*P*−1	9.4350(2)	7.7196(2)	7.6252(2)	97.213(1) 109.219(2) 89.725(2)	519.88(2)	2	[24]

*n/a – data is not available.

[62,63]. The complexes of $M[Al(BH_4)_4]$ contain the same bulky $[Al(BH_4)_4]^-$ anion with strongly deformed tetrahedral configuration, where aluminium atoms are coordinated to four BH_4^- groups via the BH_2 edges. In contrast to M⋯N bonding in $M[Al(NH_2)_4]_n$, the coordination of metal cations in $[Al(BH_4)_4]^-$ exhibits bridging M⋯H⋯B character. Moreover, the borohydride group acts like a nearly linear bridging ligand with an Al⋯B⋯M angle close to 180°. This coordination behavior is usual for the framework structures of numerous other borohydrides, like the polymorphs of $Mg(BH_4)_2$ [64,65]. These topologies are typical for coordination frameworks, highlighting the role of the borohydride anion acting as the bridging directional ligand [34].

Similarly to aluminium amides, complex anions $[Al(BH_4)_4]^-$ can be coordinated to M^+ both via corners or edges. The coordination numbers of metal cations in $M[Al(BH_4)_4]$ are similar (for Li^+, K^+, Cs^+) or higher (for Na^+) than in the corresponding $M[Al(NH_2)_4]$. The crystal structure of $NH_4[Al(BH_4)_4]$ is identical to $K[Al(BH_4)_4]$ and $Rb[Al(BH_4)_4]$, which is in accordance to the similar size of the cations. However, it also contains dihydrogen $H^{\delta+}\cdots H^{\delta-}$ bonds between protic and hydridic hydrogens of NH_4^+ and BH_4^- groups. This structural feature provokes easier hydrogen comproportionation and makes it the least stable among the $M[Al(BH_4)_4]$ compounds.

The crystal structure of $Na[Al(NH_2BH_3)_4]$ is the only one known to date for aluminium amidoboranes [24]. The central Al^{3+} atom has a tetrahedral environment formed by four nitrogen atoms from four $NH_2BH_3^-$ anions (Fig. 1), similar to aluminium amides. The Na^+ atoms are octahedrally coordinated by six BH_3 groups arising from six $NH_2BH_3^-$. This coordination is different from $M[Al(NH_2)_4]_n$, where cations are directly linked with NH_2^- groups. Thus, all $NH_2BH_3^-$ anions exhibit a bridging coordination mode linking Al^{3+} and Na^+ cations with the formation of a 3D polymer structure. Remarkably, the dihydrogen $N{-}H^{\delta+}\cdots H^{\delta-}{-}B$ bonds in $Na[Al(NH_2BH_3)_4]$ (1.96(1)–2.28(1) Å from XRPD and 1.92–2.34 Å from DFT) are close to the shortest dihydrogen bonds (1.91(5) Å) in a pristine AB [66], and significantly shorter compared to all known metal ammonia boranes (MABs) [24].

Crystal structures of molecular and cationic Al–B and Al–N complex hydrides

Most crystal structures of these two classes of compounds were characterized recently (2011–2015), see Table 2, and are based on the addition reaction between $Al(BH_4)_3$ and other hydrides, like NH_3, AB and $LiBH_4$.

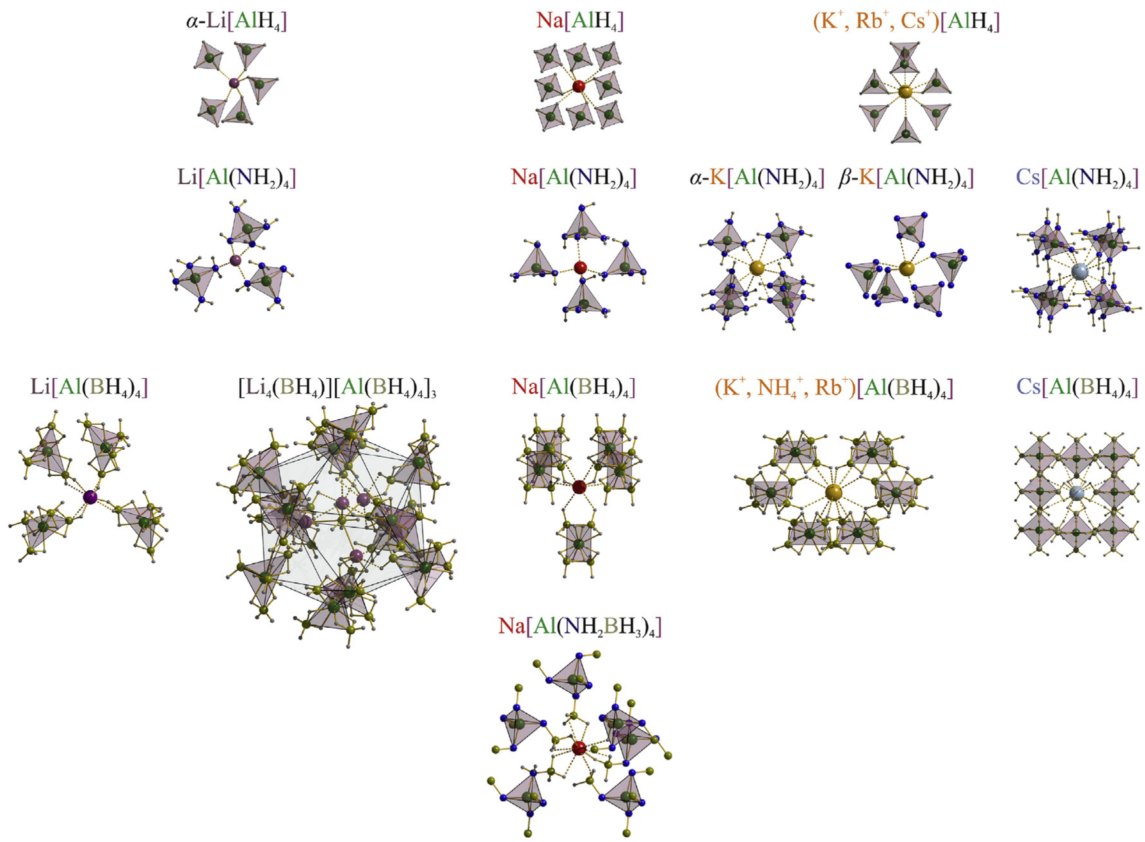

Fig. 1 – Coordination of metal cations in alanates, aluminium amides, borohydrides and amidoboranes. Aluminium-centered complex anions are shown as polyhedra.

Equimolar amounts of NH_3, AB or MeAB (methyl ammonia borane) with $Al(BH_4)_3$ result in molecular complexes $[Al(NH_3)(BH_4)_3]$, $[Al(NH_3BH_3)(BH_4)_3]$ and $[Al(CH_3NH_2BH_3)(BH_4)_3]$, see Fig. 2. Similar to the $[Al(BH_4)_4]^-$ anion, the central Al^{3+} cation is linked via BH_2 edges to three BH_4^- anions and to one molecule of NH_3, AB or MeAB. The molecule of NH_3 is linked to Al^{3+} via a nitrogen atom, which donates its lonepair electrons to Al^{3+}, while AB and MeAB are linked via BH_2 edges, all adopting a distorted tetrahedral coordination for Al^{3+}. The resulting AlH_8 polyhedron in $[Al(NH_3BH_3)(BH_4)_3]$ and $[Al(CH_3NH_2BH_3)(BH_4)_3]$ has a shape of a snub disphenoid (one of the Johnson solids), as Mg^{2+} in $Mg(BH_4)_2$ structures [64,65]. Weak dihydrogen $N{-}H^{\delta+}\cdots H^{\delta-}{-}B$ bonds associate these complexes into a 3D structure.

An increasing amount of NH_3 replaces the borohydride ligands forming hexamminealuminium (III) $[Al(NH_3)_6]^{3+}$

Table 2 – Crystal structure data for molecular and cationic Al–B and Al–N complex hydrides.

Compound	Space group	Cell parameters, Å			α, β, γ (°)	V/Å³	Z	Refs.
		a	b	c				
$[Al(NH_3)(BH_4)_3]$	$P2_1/n$	11.20(3)	11.48(3)	12.00(3)	100.9(5)	1515.0(7)	8	[50]
α-$[Al(NH_3BH_3)(BH_4)_3]$	$P2_1/c$	7.8585(2)	6.8647(1)	15.7136(8)	96.43(1)	842.36(5)	4	[25]
β-$[Al(NH_3BH_3)(BH_4)_3]$	Cc	10.8196(8)	7.2809(4)	11.3260(9)	107.7(1)	850.0(1)	4	[25]
$[Al(CH_3NH_2BH_3)(BH_4)_3]$	P−1	6.2764(3)	7.9566(5)	10.3058(8)	70.277(7) 74.744(5) 86.041(4)	467.28(6)	2	[22]
$[Al(NH_3)_6][BH_4]_3$	Pbcn	13.2824(5)	15.2698(7)	13.1848(6)		2674.14	8	[59]
$[Al(NH_3)_6][Li_2(BH_4)_5]$	P−3c	7.7978(1)	7.7978(1)	15.9693(2)		840.93(1)	2	[27]
$[Al(NH_3)_6][Li_2(BH_4)_5]\cdot 3NH_3BH_3$	F23	23.1220(3)	23.1220(3)	23.1220(3)		12361.7(5)	16	[28]
$[Al(CH_3NH_2BH_3)_2Cl_2]$ $[AlCl_4]$	Pbca	12.5826(5)	12.6510(5)	20.4039(8)		3247.9(2)	8	[22]
$[Al(CH_2NH_2)_2(BH_4)_2]\cdot[Al(BH_4)_4]$	$P2_1/c$	8.4168(5)	12.0021(7)	16.2933(12)	101.89(1)	1610.7(2)	4	[22]
$[HAl(BH_4)_2\cdot(TEDA)BH_3]_2\cdot(PhMe)_2$	$P2_1/c$	9.3652(14)	7.6214(11)	25.353(4)	99.419(3)	1785.3(5)	2	[55]
$[Cl_2AlNEt_2]_2$	Pnma	13.0763(8)	10.5499(8)	11.6434(8)		1606.3(2)	4	[56]
$[(BH_4)_2AlNEt_2]_2$	C2/c	8.7545(5)	13.0364(7)	15.9026(9)	93.884(3)	1810.8(2)	4	[56]
$[H(Cl)AlNEt_2]_2$	Pnma	12.0647(8)	10.4815(6)	11.4958(7)		1453.7(2)	4	[56]
$[H(BH_4)AlNEt_2]_2$	Pnma	12.1579(14)	10.3264(12)	12.2729(14)		1540.8(3)	4	[56]

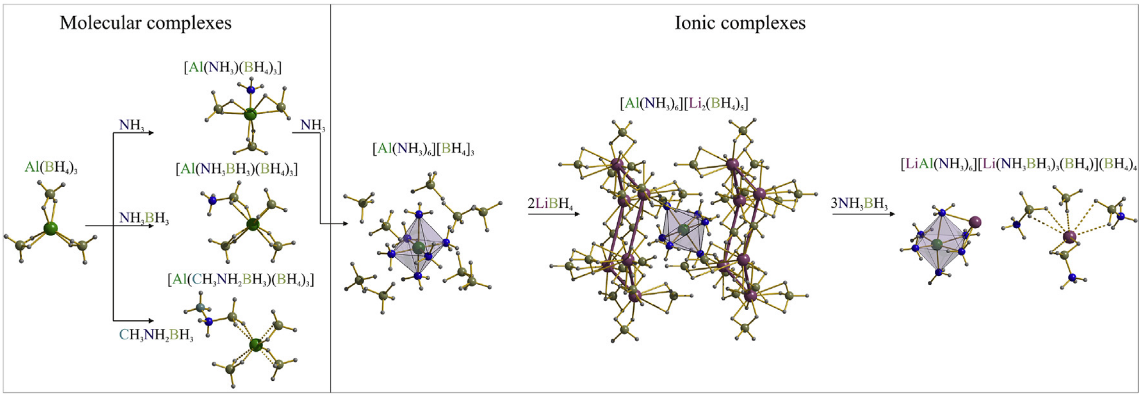

Fig. 2 – Sequence of addition reactions to $Al(BH_4)_3$ leading first to molecular complexes and then to Al-centered complex cations. Color code: Al-green, N-blue, C-teal, B-olive, H-grey. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

complex cation, passing from the molecular structure to ionic. This complex cation has a distorted octahedral coordination of Al^{3+}, linked exclusively with six NH_3 ligands via nitrogen atoms. The hexamminealuminium cations in $[Al(NH_3)_6][BH_4]_3$ are surrounded by free BH_4^- anions, connected with NH_3 by dihydrogen bonds at 1.91–2.19 Å.

The insertion of $LiBH_4$ into $[Al(NH_3)_6][BH_4]_3$ yields a Li-based anion and the resulting formula $[Al(NH_3)_6][Li_2(BH_4)_5]$ [27]. The $[Al(NH_3)_6]^{3+}$ complex cation remains in the structure without significant changes and Li^+ adopts tetrahedral coordination by four BH_4^- groups in line with lithium borohydride crystal chemistry [73]. These $Li[BH_4]_4$ tetrahedra are then vertex-linked through three bridging BH_4^- units with the fourth one in the trans position, leading to the formation of a two-dimensional honeycomb-patterned sheet, see Fig. 2 [27]. This structural topology is similar to borohydride structures, as in $Mg(BH_4)_2$ polymorphs [64,65], as well as to that of some porous silicate zeolites [74]. As in $Na[Al(NH_2BH_3)_4]$, the closest $N{-}H^{\delta+}\cdots H^{\delta-}{-}B$ interactions in $[Al(NH_3)_6][Li_2(BH_4)_5]$ are even shorter than those in MABs and are comparable to those in the solid ammonia borane, NH_3BH_3 [24,66].

Interestingly, $[Al(NH_3)_6][Li_2(BH_4)_5]$ is not the last member of the addition sequence (Fig. 2), as it reacts further with AB forming $[Al(NH_3)_6][Li_2(BH_4)_5]\cdot 3NH_3BH_3$. Al^{3+} is identically co-ordinated to six ammonia atoms in hexamminealuminium (III) complex cation. On the contrary, the coordination behavior of Li atoms changes dramatically: one Li^+ is coordinated to $[Al(NH_3)_6]^{3+}$ octahedron via the face, while the other Li^+ adopts tetrahedral coordination with one BH_4^- and three molecules of AB. Non-coordinated BH_4^- anions fill the space in the vicinity of $[Al(NH_3)_6]^{3+}$, forming H⋯H dihydrogen bonds with NH_3 and AB molecules. The intermolecular H⋯H distances of 1.90 and 1.79 Å are found to be slightly shorter than those in the recently discovered ammine metal borohydrides (AMBs) and MABs [75]. Given the description above, the formula of this compounds is better written as $[LiAl(NH_3)_6][Li(NH_3BH_3)_3(BH_4)](BH_4)_4$.

The examples of complex hydrides where aluminium atoms are centering both the complex cation and anion are quite rare. Indeed, only two structures of "autoionized" Al-based hydrides, $[Al(CH_3NH_2BH_3)_2Cl_2][AlCl_4]$ and $[Al(CH_2NH_2)_2(BH_4)_2][Al(BH_4)_4]$, were recently investigated, see Fig. 3.

MeAB ligand coordinates to Al^{3+} via bridging hydrogens of the BH_3 groups with Al⋯B and Al–H distances of 2.24(5)–2.26(4) and 1.8(2)–1.9(2) Å, which are similar to the ones in molecular $[Al(NH_3BH_3)(BH_4)_3]$ and $[Al(CH_3NH_2BH_3)(BH_4)_3]$ complexes. The Al⋯Cl distances of 2.11(1) and 2.14(1) Å in the $[Al(CH_3NH_2BH_3)_2Cl_2]^+$ cation are in a good agreement with 2.1–2.3 Å from other known cationic complexes of Al [76].

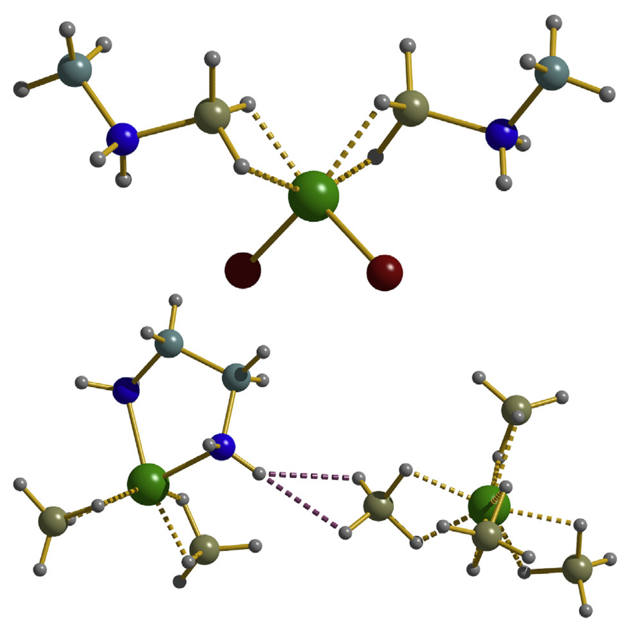

Fig. 3 – The fragments of the autoionized complexes $[Al(CH_3NH_2BH_3)_2Cl_2][AlCl_4]$ (top) and $[Al(CH_2NH_2)_2(BH_4)_2][Al(BH_4)_4]$ (bottom). The complex cation $[Al(CH_2NH_2)_2(BH_4)_2]^+$ and anion $[Al(BH_4)_4]^-$ are linked via bifurcated dihydrogen bond (dashed violet). Color code: Al-green, Cl-brown, N-blue, C-teal, B-olive, H-grey. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

$[Al(CH_2NH_2)_2(BH_4)_2][Al(BH_4)_4]$ is the only autoionized Al-borohydride complex known so far. Each of its ions adopts a distorted tetrahedral coordination for Al atoms. The N···Al···N angle of 86.5(2)° is similar the other known bidentate chelates of Al [76]. The geometry of a slightly flattened tetrahedron for $[Al(BH_4)_4]^-$ complex anion is also identical to those in M $[Al(BH_4)_4]$ (M = Li^+, Na^+, K^+, NH_4^+, Rb^+, Cs^+) and $[Ph_3MeP]$ $[Al(BH_4)_4]$ [22,77].

$[Al(CH_2NH_2)_2(BH_4)_2]^+$ is a chelate, where Al atom is linked via N atoms to the same ethylenediamine molecule, and via BH_2 edges to two BH_4^- groups, see Fig. 3. Al···B distances of 2.16(7) and 2.17(8) Å in the cation are slightly shorter than 2.23(8)–2.27(8) Å Al···B distances in $[Al(BH_4)_4]^-$. The Al···N distances of 1.95(4) and 1.96(4) Å are typical (1.9–2.0 Å) for other Al-containing cations [76]. Similarly to the molecular $[Al(NH_3BH_3)(BH_4)_3]$ and $[Al(CH_3NH_2BH_3)(BH_4)_3]$, the crystal structure of $[Al(CH_2NH_2)_2(BH_4)_2][Al(BH_4)_4]$ contains both simple and bifurcated dihydrogen N–$H^{\delta+}$ ... $H^{\delta-}$–B bonds with H···H distances of 2.02–2.22 Å and H···H–N angles of 140–160°.

Molecular hydride complexes of Al can also take a dimeric form, forming $(Al–H)_2$ and $(Al···N)_2$ four-membered rings [55,56]. The bridging Al–$(\mu\text{-}H)_2$–Al is present in the crystal structure of $[HAl(BH_4)_2\cdot(TEDA)BH_3]_2(PhMe)_2$, see Fig. 4a [55]. Similar Al–(μ-H)–Al units have been proposed for $[HAl(BH_4)_2]_n$ from NMR and IR spectroscopy data [78]. The reported interatomic distances Al···N, Al···B, B···N and Al–H (with BH_4^-) are similar to those in $M[Al(BH_4)_4]$ and $[Al(NH_3BH_3)(BH_4)_3]$. The Al–H distance with the bridging hydrogen is slightly shorter, 1.72 Å, than the Al–H bond with the BH_4^- group of around 1.82 Å. It was surmised that the crystal structure might be stabilized by π-interactions and weak dihydrogen N–$H^{\delta+}$ ... $H^{\delta-}$–B bonds with H···H distances of ~2.7–2.9 Å [55].

The crystal structures of $[X_2AlNEt_2]_2$ and $[H(X)AlNEt_2]_2$ (X = Cl^-, BH_4^-) contain $(Al–N)_2$ four-membered rings [56], see Fig. 4b and c. The Al–N–Al–N torsion angles showed the stronger deviation from planarity in the presence of chlorine ligands due to the steric and electron drawing effect on Al atoms [56].

Thermal decomposition and hydrogen storage properties of Al–B and Al–N complex hydrides

Thermal properties of complex hydrides with Al–B and Al–N anions

$M[Al(NH_2)_4]_n$ complexes show peaks of ammonia release at temperatures from 70 to 160 °C [19]. The decomposition temperatures for $M[Al(NH_2)_4]_n$ series increases with the electronegativity of M, i.e. from K to Li and from Ca to Mg. This trend is opposite for metal borohydrides, $M(BH_4)_n$ [79,80], as well as for Al-based bimetallic series, $M[Al(BH_4)_4]$, as will be discussed below. The opposite trends apparently reflect different mechanisms of the decomposition of the amide and borohydride series.

There are several interpretations regarding the thermal decomposition pathway of alkali metal aluminium amides. The most detailed investigation has been done for $Li[Al(NH_2)_4]$. The first attempt to explain the thermal decomposition of Li

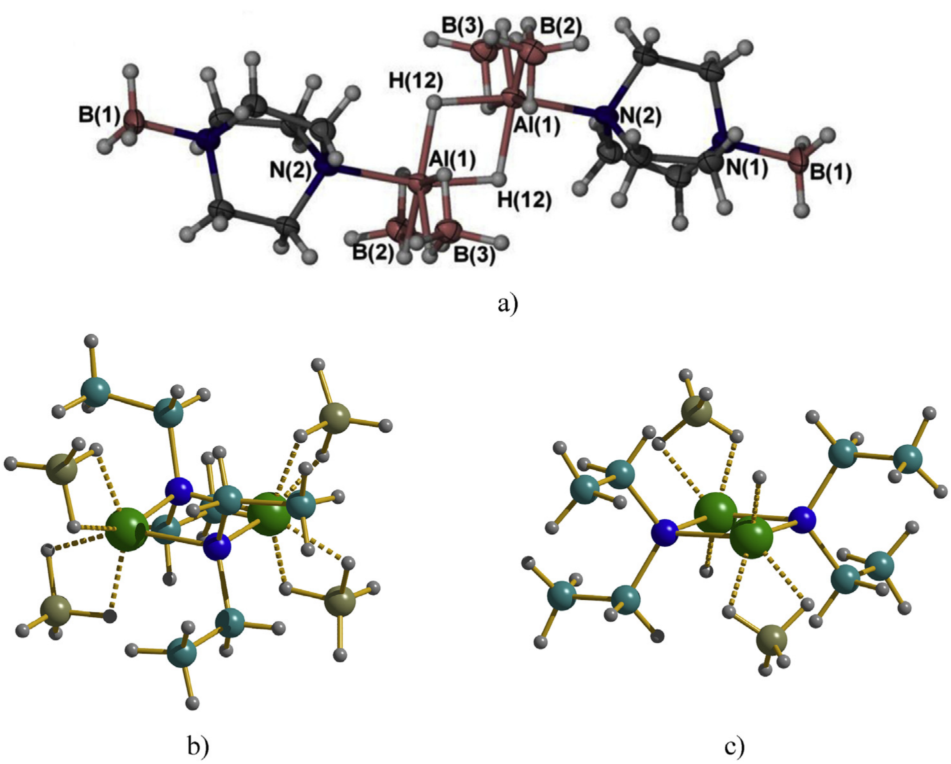

Fig. 4 – Dimeric molecular structures of $[HAl(BH_4)_2\cdot(TEDA)BH_3]_2(PhMe)_2$ [55] (a), $[(BH_4)_2AlNEt_2]_2$ (b) and $[H(BH_4)AlNEt_2]_2$ (c). Color code for (b) and (c): Al-green, N-blue, C-teal, B-olive, H-grey. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

$[Al(NH_2)_4]$ was made in 1960s by Rouxel and Brec [81], stating the following scheme:

$$\begin{aligned} Li[Al(NH_2)_4] &\rightarrow LiAl(NH)_2 + 2NH_3 && (160-185\,^{\circ}C) \\ &\rightarrow 1/3Li_3AlN_2 + 2/3AlN + 8/3NH_3 && (>185\,^{\circ}C) \end{aligned} \tag{26}$$

Jacobs at al. proposed another scheme, via formation of $LiNH_2$ [67]:

$$\begin{aligned} Li[Al(NH_2)_4] &\rightarrow LiNH_2 + 1/2Al_2(NH)_3 + 3/2NH_3 && (160-185\,^{\circ}C) \\ &\rightarrow LiNH_2 + AlN + 2NH_3 && (>280\,^{\circ}C) \\ &\rightarrow 1/3Li_3AlN_2 + 2/3AlN + 8/2NH_3 && (>400\,^{\circ}C) \end{aligned} \tag{27}$$

More recent investigation from Eymery et al. combines some part from the scheme (22), but the final Li-containing species correspond to the amorphous Li_2NH [82]:

$$\begin{aligned} Li[Al(NH_2)_4] &\rightarrow LiAl(NH)_2 + 2NH_3 && (>130\,^{\circ}C) \\ &\rightarrow LiNH_2 + AlN + 2NH_3 && (>130\,^{\circ}C) \\ &\rightarrow 1/2Li_2NH + AlN + 5/2NH_3 && (>400\,^{\circ}C) \end{aligned} \tag{28}$$

Formation of the crystalline and amorphous Li_3AlN_2 and AlN have been confirmed by recent experimental works [83,84], in favor of the schemes (22) and (23). The question regarding the Li–Al–N–H intermediate(s) at the first decomposition step is also complicated. Possible formation of various $[NH_n]^{n-3}$ anions was suggested upon the thermal decomposition [83,84]:

$$\begin{aligned} 3Li[Al(NH_2)_4] &\rightarrow Li_3Al_3(NH_2)_{12-2l}(NH)_l + lNH_3 && (<\sim 160\,^{\circ}C;\ 0 \le l \le 4) \\ &\rightarrow Li_3Al_3(NH_2)_{4-m}(NH)_{4-m}N_m + (4+m)NH_3 && (>\sim 160\,^{\circ}C;\ 0 \le m \le 4) \\ &\rightarrow (1-n)Li_3AlN_2 + 2(1-n)AlN + Li_{3n}Al_{3n}N_{4n} + 8NH_3 && (>500\,^{\circ}C;\ 0 \le n \le 1) \end{aligned} \tag{29}$$

Despite the lack of hydrogen evolution from the pristine $M[Al(NH_2)_4]_n$ complexes, the interest remains in their RHCs with other metal hydrides. In particular, $Li[Al(NH_2)_4]$–4LiH composite showed hydrogen desorption already at room temperature, according to the proposed reaction [85]:

$$Li[Al(NH_2)_4] + 4LiH \rightarrow LiAl(NH)_2 + 2Li_2NH + 4H_2 \tag{30}$$

Similarly to the decomposition intermediates for the pristine $Li[Al(NH_2)_4]$, the nature of the $LiAl(NH)_2$ metastable compound remains unclear. The poor reversibility of the composite was explained by the rapid decomposition of this intermediate into AlN, which is found to be inactive with respect to rehydrogenation at the applied conditions (130 °C and 20 bar of H_2) [85]. Further investigations of the aluminium based amides can yield new composites of storing larger amounts of hydrogen at temperatures around 100 °C.

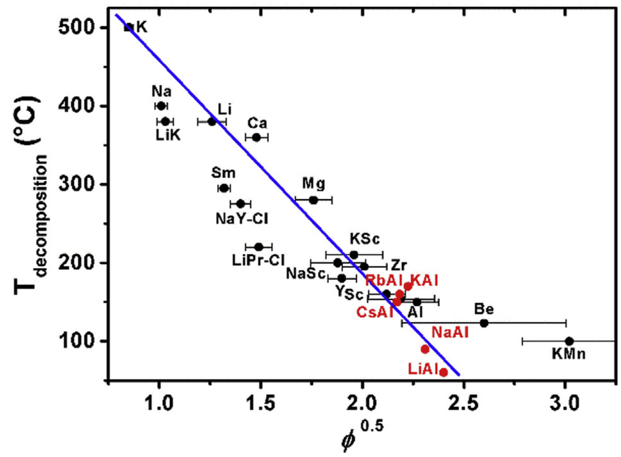

Fig. 5 – The experimental decomposition temperatures of metal borohydrides as a function of ionic potential obtained using dynamical charges on cations. The values for $M[Al(BH_4)_4]$ ($M = Li^+, Na^+, K^+, Rb^+, Cs^+$) are shown as red circles, while the data shown in black circles were taken from Ref. [86]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The experimental decomposition temperatures of $M[Al(BH_4)_4]$ ($M = Li^+, Na^+, K^+, Rb^+, Cs^+$) linearly correlates with the square root of their ionic potential $\varphi^{0.5}$ on M, calculated from the dynamical charges, see Fig. 5 [22]. This parameter gives a more linear correlation with the decomposition temperatures than the Pauling electronegativity, χ_P. $NH_4[Al(BH_4)_4]$ does not fall on in this line, because the recombination of hydrogens from NH_4^+ and BH_4^- lowers significantly the stability of this compound.

In terms of thermal decomposition properties, the family of $M[Al(BH_4)_4]$ ($M = Li^+, Na^+, K^+, NH_4^+, Rb^+, Cs^+$) and $[Li_4(BH_4)][Al(BH_4)_4]_3$ can be separated into several groups: the decomposition of light (Li^+, Na^+), medium (K^+), heavy (Rb^+, Cs^+) and proton-containing (NH_4^+) aluminium borohydrides.

The light $M[Al(BH_4)_4]$ ($M = Li^+, Na^+$) decompose below 100 °C with the evolution of molecular $Al(BH_4)_3$ [22,41,87]:

$$M[Al(BH_4)_4] \rightarrow MBH_4 + Al(BH_4)_3\ (M = Li^+, Na^+) \tag{31}$$

Interestingly, $Li[Al(BH_4)_4]$ decomposes into $[Li_4(BH_4)][Al(BH_4)_4]_3$ at the first step and the latter gives the starting $LiBH_4$ and the rest of $Al(BH_4)_3$ [22]:

$$[Li_4(BH_4)][Al(BH_4)_4]_3 \rightarrow 4LiBH_4 + 3Al(BH_4)_3 \quad (32)$$

$$4Li[Al(BH_4)_4] \rightarrow [Li_4(BH_4)][Al(BH_4)_4]_3 + Al(BH_4)_3 \quad (33)$$

$K[Al(BH_4)_4]$ decomposes at around 160 °C and two different decomposition schemes have been proposed. Among the possible decomposition reactions, one is identical to the decomposition of the light alkali metal aluminium borohydrides (27), with evolution of $Al(BH_4)_3$ and formation of KBH_4 [42,43]. Due to the evolution of hydrogen and diborane during thermal decomposition and due to lower mass losses than expected for $Al(BH_4)_3$ abstraction, a different decomposition pathway has been proposed according to the following reaction [21]:

$$2K[Al(BH_4)_4] \rightarrow KBH_4 + \text{amorphous “}KAl_2B_3\text{”} + 2B_2H_6 + 8H_2 \quad (34)$$

The thermal decomposition of heavy $M[Al(BH_4)_4]$ ($M = Rb^+$, Cs^+) gives the lowest mass losses. The presence of hydrogen and diborane was confirmed by thermogravimetric analysis coupled with mass spectrometry analysis of evolving gases (TGA–MS), however the decomposition scheme is not defined with certainty [22]. Remarkably, $Cs[Al(BH_4)_4]$ evolves the most pure hydrogen in the $M[Al(BH_4)_4]$ series, at temperatures below 160 °C.

$NH_4[Al(BH_4)_4]$ decomposes in two steps [22], at about 35 °C and 58 °C. A similar two-step thermal decomposition was found for $[Al(NH_3BH_3)(BH_4)_3]$ [25], which will be discussed later. According to the TGA–MS data, $NH_4[Al(BH_4)_4]$ releases hydrogen, diborane and ammonia at both decomposition steps. The solution ^{11}B and ^{27}Al NMR spectra showed also the signals of diborane, $Al(BH_4)_3$, $Al(BH_4)_3 \cdot NHBH$ and $[HAl(BH_4)_2]$ [22,25].

The Al-based bimetallic compounds combining even stronger polarizing Mg^{2+} or Ca^{2+} cations, would lead to the decomposition at room temperature, and thus are most likely unstable under ambient conditions. Indeed, the attempts to isolate bimetallic borohydrides of the $Mg(BH_4)_2 \cdot Al(BH_4)_3$ and $Ca(BH_4)_2 \cdot Al(BH_4)_3$ systems were unsuccessful [22]. Consequently, the family of Al-based borohydrides is likely limited to the alkali metal and ammonium series. With the diversity of the decomposition pathways and the varied stability, the aluminium borohydride chemistry can be developed in terms of reactive hydride composites based on $M[Al(BH_4)_4]$, similarly to $M[Al(NH_2)_4]_n$. As we mentioned above in this subchapter, the $M[Al(NH_2)_4]_2$ ($M = Mg^{2+}$, Ca^{2+}) series is on the contrary stable, with higher stability for the strongest polarizing Mg^{2+}.

$Na[Al(NH_2BH_3)_4]$ is a completely different representative possessing an Al-based complex anion, since it has an anion containing intermolecular dihydrogen $N–H^{\delta+} \ldots H^{\delta-}–B$ bonds. The thermal decomposition of $Na[Al(NH_2BH_3)_4]$ occurs in two steps at around 120 and 160 °C and reveals the formation of only one crystalline phase, $NaBH_4$ [24]. The FTIR spectrum of the final residue shows characteristic bands of $NaBH_4$ and a number of additional bands suggesting the presence of the Al–N, B–N, B–H and N–H bonds. Using TGA–MS and volumetric data on the decomposition of $Na[Al(NH_2BH_3)_4]$, the overall reaction was suggested:

$$Na[Al(NH_2BH_3)_4] \rightarrow NaBH_4 + AlN_4B_3H_{(0\div1.8)} + (6.2\div8.0)H_2 \quad (35)$$

Remarkably, a slow hydrogen absorption was observed at 250 °C for the completely decomposed samples of $Na[Al(NH_2BH_3)_4]$ [24]. About 1.7 out of 6.2 mol (~27%) of the released hydrogen has been readsorbed by the amorphous residue. This reversible absorption presumably corresponds to the reversibility of the second decomposition step (at 160 °C) [24].

$Na[Al(NH_2BH_3)_4]$ forms quantitatively in the $NaAlH_4–4NH_3BH_3$ system, releasing 4 equivalents of hydrogen. Various composites between alanates and AB can be considered in a broader context. In particular, $MAlH_4–NH_3BH_3$ ($M = Li^+$, Na^+) [88] as well as $Li_3AlH_6–nNH_3BH_3$ ($3 \le n \le 6$) composites have been intensively investigated [48,89]. Hydrogen desorption from $MAlH_4–NH_3BH_3$ ($M = Li^+$, Na^+) starts already at 53 and 66 °C, respectively, where the formation of the $[Al(NH_2BH_3)_4]^-$ anion is confirmed [24]. The peak of hydrogen release from various $Li_3AlH_6–nAB$ composites is in the range of 50–72 °C [48,89]. For the interaction between Li_3AlH_6 and AB, two possible scenarios have been suggested [48,89]. First, solid state NMR data indicate that $Li_3AlH_6–3NH_3BH_3$ composite undergoes a formation of $(LiAB)_x(AB)_{1-x}$ at the temperatures as low as 50 °C and a subsequent polymerization [89]. Second, the recent investigation of $Li_3AlH_6–4NH_3BH_3$ suggested the formation of a mixed-metal amidoborane, with a proposed composition $Li_3AlH_2(NH_2BH_3)_4$ [48]. 9 wt% of hydrogen evolves from $Li_3AlH_6–4NH_3BH_3$ within 200 min at 130 °C [48]. The TGA and MS data also confirmed the high purity of hydrogen from the $Li_3AlH_6–nNH_3BH_3$ (n = 4 and 5) composites, highlighting an effective suppression of multiple volatile byproducts of ammonia, borazine and aminoborane NH_2BH_2, which is usual for the dehydrogenation of pristine AB [90,91]. Moreover, the hydrogen desorption capacity of the $Li_3AlH_6–4NH_3BH_3$ system can be regenerated with 35% yield by a chemical treatment with hydrazine [48].

Thermal properties of molecular and cation Al–B and Al–N complex hydrides

Most examples of these two classes of materials contain protic and hydridic hydrogens present in $N–H^{\delta+}$ and $B–H^{\delta-}$ groups, whereby this combination favors hydrogen release at moderate temperatures. Numerous composites with chemical hydrides, such as AB, have been intensively studied and showed good dehydrogenation properties.

The molecular complex $[Al(NH_3BH_3)(BH_4)_3]$ demonstrates two decomposition steps: the first starts at ~60 °C and finishes at ~80 °C, the second is centered around 90 °C, see Table 3 [25]. The first step is endothermic (39 kJ/mol) and can be separated from the second by carrying out the reaction at 70 °C. Remarkably, TGA–MS data, volumetric analysis and solution ^{11}B with ^{27}Al NMR confirmed the evolution of 2 mol of pure hydrogen at 70 °C in accordance with a reaction:

Table 3 – Hydrogen storage properties for $Al(BH_4)_3$ complexes with AB [25] and ethylenediamine [51].

Compound/Composite	H_2 release (wt%)	H_2 purity (wt%)	T_{dec} peak 1 T (°C)	T_{dec} peak 2 T (°C)
$[Al(NH_3BH_3)(BH_4)_3]$	3.91	Close to 100	60	90
$Al(BH_4)_3 \cdot C_2H_8N_2$	10.4	99.9	125	198
$Al(BH_4)_3 \cdot 2C_2H_8N_2$	9.4	99.6	135	197
$Al(BH_4)_3 \cdot 3C_2H_8N_2$	8.7	99.5	145	197
$Al(BH_4)_3 \cdot 4C_2H_8N_2$	8.4	96.1	149	197

$$[Al(NH_3BH_3)(BH_4)_3] \rightarrow 1/n\ [Al(NHBH)(BH_4)_3]_n + 2H_2 \quad (36)$$

This favorable decomposition pathway, endothermic dehydrogenation and low decomposition temperature, make this system an attractive model for efficient hydrogen elimination from AB. $Al(BH_4)_3$ works as a unique mild Lewis acid, which coordinates both the starting and the dehydrogenated BH_n groups ($n = 1, 3$). In perspective, other Al-based Lewis acids, less challenging with respect to stability and safety than aluminium borohydride, can be used for the dehydrogenation of AB and its derivatives.

The series of $Al(BH_4)_3 \cdot nC_2H_8N_2$ ($1 \leq n \leq 4$) have also been characterized in terms of hydrogen storage properties [51], the details of which are shown in Table 3. Two-step dehydrogenation is typical for these complexes, where H_2 is the predominant product according to the MS experiments. According to the temperature-programmed desorption, half of the total amount of H_2 is released during the first step; the amount of hydrogen released increases with n. It was pointed out that the C–H bond was not involved in the dehydrogenation of the complex. It was suggested that one of the two amino groups combines with some of the BH_4^- anions through the recombination of $N{-}H^{\delta+}{\cdots}H^{\delta-}{-}B$ dihydrogen bonds, while the second amino group reacts with BH_4^- at higher temperatures.

The cation complex $[Al(NH_3)_6][BH_4]_3$ along with its derivatives and numerous composites with $LiBH_4$ and AB has attracted significant attention by the hydrogen storage community, see Table 4. The pristine $[Al(NH_3)_6][BH_4]_3$ and its

Table 4 – Some hydrogen storage properties of $Al(BH_4)_3$-based ammoniates and their composites with AB and metal borohydrides.

Compound/Composite	H_2 release (wt%)	H_2 purity (wt%)	T_{dec} peak (°C)	Main impurity	Refs.
$[Al(NH_3)_6][BH_4]_3$	11.8	67.4	168	NH_3	[26,58]
$Al(BH_4)_3 \cdot 5NH_3$	16.8	90.6	159	NH_3	[58]
$Al(BH_4)_3 \cdot 4NH_3$	15.5	>99	128	–	[58]
$Al(BH_4)_3 \cdot 3NH_3$	13.7	>99	113	–	[58]
$Al(BH_4)_3 \cdot 2NH_3$	13.7	66.7	108	B_2H_6	[58]
$[Al(NH_3)_6][BH_4]_3–2LiBH_4$	15.5	79.0	138	NH_3	[27,58]
$[Al(NH_3)_6][Li_2(BH_4)_5]$	15.1	94.3	125, 190–300	NH_3	[28]
$Al(BH_4)_3 \cdot 5NH_3–LiBH_4$	15.4	81.0	145	NH_3	[58]
$Al(BH_4)_3 \cdot 5NH_3–2LiBH_4$	15.8	92.4	142	NH_3	[58]
$Al(BH_4)_3 \cdot 4NH_3–LiBH_4$	16.1	>99	109, 128	–	[58]
$Al(BH_4)_3 \cdot 4NH_3–2LiBH_4$	14.2	96.6	121	B_2H_6	[58]
$[Al(NH_3)_6][BH_4]_3–0.5\ Mg(BH_4)_2$	11.2	100[a]	130[b]	–	[59]
$[Al(NH_3)_6][BH_4]_3–0.5Ca(BH_4)_2$	10.9	99.2[a]	130[b]	NH_3	[59]
$[Al(NH_3)_6][Li_2(BH_4)_5]–0.5\ Mg(BH_4)_2$	12.4	99.0[a]	130[b]	NH_3	[59]
$[Al(NH_3)_6][BH_4]_3–NH_3BH_3$	13.8	96.4	?	?	[28]
$[Al(NH_3)_6][BH_4]_3–2NH_3BH_3$	14.2	97.3	?	?	[28]
$[Al(NH_3)_6][BH_4]_3–3NH_3BH_3$	14.4	98.1	?	?	[28]
$[Al(NH_3)_6][BH_4]_3–4NH_3BH_3$	14.5	98.3	119, 154	NH_3	[28]
$[Al(NH_3)_6][BH_4]_3–5NH_3BH_3$	14.7	98	?	?	[28]
$[Al(NH_3)_6][BH_4]_3–6NH_3BH_3$	14.8	97.8	?	?	[28]
$[Al(NH_3)_6][Li_2(BH_4)_5]–NH_3BH_3$	16.5	97.6	?	?	[28]
$[Al(NH_3)_6][Li_2(BH_4)_5]–2NH_3BH_3$	16.6	98	?	?	[28]
$[Al(NH_3)_6][Li_2(BH_4)_5] \cdot 3NH_3BH_3$	16.9	98.6	105, 125	NH_3	[28]
$[Al(NH_3)_6][Li_2(BH_4)_5]–4NH_3BH_3$	16.8	97.1	?	?	[28]
$[Al(NH_3)_6][Li_2(BH_4)_5]–5NH_3BH_3$	16.6	96.9	?	?	[28]
$[Al(NH_3)_6][Li_2(BH_4)_5]–6NH_3BH_3$	16.4	95	?	?	[28]
$[Al(NH_3)_6][Al(NH_2BH_3)_6]$	10.3	99.5[a]	105	NH_3	[60]

? Not mentioned in the literature.
— no detectable impurities.
[a] Isothermal treatment of the samples.
[b] The capacity and purity of the H_2 emission gas were determined using gravimetric and volumetric results, with the assumption that the only impurity was NH_3.

composite with 2 mol of $LiBH_4$ release hydrogen contaminated significantly by NH_3 [26]. The second problem is related to poor dehydrogenation kinetics under moderate temperatures [26]. These disadvantages were eliminated by decreasing the ammonia content in the starting complex. This decreases the H_2 desorption temperature and improves the purity of the released gas, especially for $H^{\delta+}/H^{\delta-}$ ratios in the composites close to one, the latter corresponds to 4:3 NH_3/BH_4^- molar ratio, see Table 4 [58]. The second parameter influencing hydrogen purity and the desorption temperature is the addition of other metal borohydrides [59]. In particular, $Mg(BH_4)_2$ has the most remarkable impact on the purity of the released hydrogen both for $[Al(NH_3)_6][BH_4]_3$ and $[Al(NH_3)_6][Li_2(BH_4)_5]$. This phenomenon was explained by the high polarizing power of Mg^{2+}, which helps to compensate a relatively low polarizing power of the large $[Al(NH_3)_6]^{3+}$ cation. It was suggested that the added cations activate the borohydride to such an extent that its hydridic hydrogens react with the protons of $[Al(NH_3)_6]^{3+}$ cation [59]. Another possible mechanism is that strongly polarizing cations can coordinate and thus destabilize the ammonia complex $[Al(NH_3)_6]^{3+}$.

Numerous composites of $[Al(NH_3)_6][BH_4]_3$ and $[Al(NH_3)_6][Li_2(BH_4)_5]$ with AB have been investigated [28]. The addition of AB significantly lowered the onset temperature of gas evolution. The most enhanced hydrogen purity and release kinetics was observed for $[Al(NH_3)_6][BH_4]_3{-}4NH_3BH_3$ composite and for $[Al(NH_3)_6][Li_2(BH_4)_5]\cdot 3NH_3BH_3$ [28]. The H_2 evolution results from the interaction between AB and NH_3 of the $[Al(NH_3)_6]^{3+}$ cation [28].

In order to facilitate the dehydrogenation kinetics and regeneration of $[Al(NH_3)_6][BH_4]_3$, its composites with AB and $LiBH_4$ were synthesized and a nanoconfinement strategy was also applied [28,92]. A hypercross-linked porous polymer of poly(styrene-co-divinylbenzene) (PSDB) resin was used as a nanosupport. The phenyl rings of the PSDB resin interact with the Lewis-acidic metal cations, such as Al^{3+} in the initial $Al(BH_4)_3$, and then lead to their anchoring. Subsequent treatment with ammonia yields well-distributed $[Al(NH_3)_6][BH_4]_3$ [28,92]. The nanosized $Al(BH_4)_3$-based materials featured an advanced hydrogen-storage performance well beyond that of its bulk counterpart. This strategy gives dehydrogenation with high purity (>99 mol%, for $[Al(NH_3)_6][BH_4]_3$) and superior kinetics [28,92]. More importantly, dehydrogenated $[Al(NH_3)_6][BH_4]_3$/PSDB was partly regenerated by hydrazine, and the rehydrogenated material can be again dehydrogenated [92].

The autoionized complex $[Al(NH_3)_6][Al(NH_2BH_3)_6]$ decomposes in the range of 65–180 °C [60]. It gives different decomposition products under inert gas flow and in a closed vessel in accordance with the following equations, respectively:

$$[Al(NH_3)_6][Al(NH_2BH_3)_6] \rightarrow 2AlN_3B_3H_3 + 6NH_3 + 12H_2 \quad (37)$$

$$[Al(NH_3)_6][Al(NH_2BH_3)_6] \rightarrow 2AlN_6B_3H_{6.5} + (8.5{-}9.0)H_2 \quad (38)$$

The XPS characterization of the remaining species of $AlN_3B_3H_3$ suggests the formation of an Al–N–B matrix with anticipated borazine-like structure [60]. On the other hand, $AlN_6B_3H_{6.5}$ contains boron atoms with a BN_3 or BN_2H environment, which proves a different decomposition mechanism in a closed system.

Composition-structure-property relations

The comparison of the decomposition temperatures and hydrogen purities for the homoleptic Al-based complexes points to the improved properties for the systems containing both protic and hydridic hydrogens, namely $H^{\delta+}$ and $H^{\delta-}$ connected to N and B atoms respectively. Despite the fact that hydrogen desorption can originate also from homopolar $H^{\delta+}\cdots H^{\delta+}$ and $H^{\delta-}\cdots H^{\delta-}$ interactions [93], the anionic $M[Al(NH_2)_4]_n$ and $M[Al(BH_4)_4]$ (M = alkali metal for $n = 1$, and alkali earth metal, for $n = 2$) in their pure form desorb ammonia, diborane and even $Al(BH_4)_3$. However, due to the high H-capacity, they are interesting as potential components of RHCs in combination with other hydrides, containing the counter-charged hydrogens. In particular, it would be interesting to characterize RHCs based on mixtures of $M[Al(NH_2)_4]_n$ with $M[Al(BH_4)_4]$. The formation and properties of amide-borohydride complexes like $M[Al(BH_4)_{4-x}(NH_2)_x]$ should also be explored. The first amide-borohydride containing aluminium, $Li_2(BH_4)[Al(ND_2)_4]$, was reported during the revision of this manuscript [94]. Interestingly, Al^{3+} coordinates only amides while the borohydride anions interact with the Li^+ cation. The presence of boron and nitrogen atoms allows the formation of the unique decomposition products prone to rehydrogenation, direct or with the help of hydrazine [95]. Good examples are the products obtained by dehydrogenation of $Na[Al(NH_2BH_3)_4]$ [24] and of $Li_3AlH_6{-}4NH_3BH_3$ [48] systems.

Desorption of pure hydrogen at mild conditions is favored by the presence of $H^{\delta+}$ and $H^{\delta-}$. However, the existence of the dihydrogen bonds $H^{\delta+}\cdots H^{\delta-}$ in the structure of the starting hydride is not a prerequisite. An example is $Li_4(BH_4)(NH_2)_3$ containing no dihydrogen bonds [96] but desorbing pure hydrogen at around 100 °C [97]. It would be interesting to analyze the correlation between the length of the $H^{\delta+}\cdots H^{\delta-}$ contacts and the decomposition temperature. In Fig. 6, we plot data for all Al-based complexes with known crystal structures

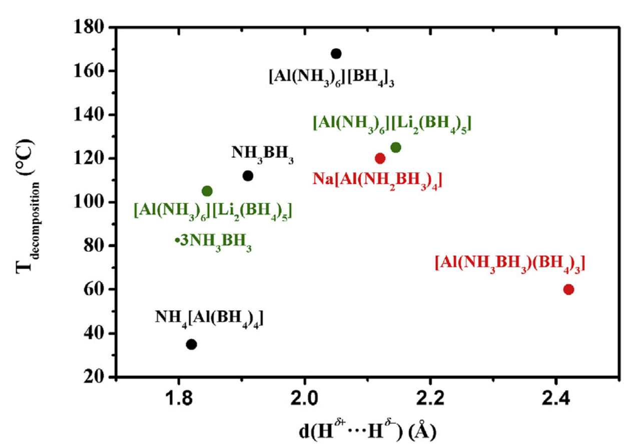

Fig. 6 – Stability of Al complexes of B- and N-based hydrides versus average dihydrogen bonds lengths. The colors indicate the hydrogen purity: black – low, green –higher than 94 wt%, red – no impurities have been detected. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

containing dihydrogen bonds, along with the pristine AB for comparison. As can be expected, compounds with the shortest $H^{\delta+}\cdots H^{\delta-}$ bonds are less stable, probably due to the easy recombination of hydrogens to form H_2. The dihydrogen bonds of 2.0–2.1 Å correspond to the maximum in stability of the hydrides. Although the latter observation is not rigorous considering the number of the experimental points, it is clear from the mechanistic considerations that not all dihydrogen bonds are favoring direct hydrogen splitting on heating, but all of them are stabilizing the initial complex.

Note that short dihydrogen bonds do not ensure the formation of pure hydrogen. An important parameter is also a ratio of protic and hydridic atoms $H^{\delta+}/H^{\delta-}$, because a significant excess of protic or hydridic hydrogens creates different impurities: protic – ammonia, hydridic – diborane or others, such as $Al(BH_4)_3$. $[Al(NH_3)_6][Li_2(BH_4)_5]$ and $[Al(NH_3)_6][Li_2(BH_4)_5]\cdot 3NH_3BH_3$ contain almost equal numbers of protic and hydridic hydrogens and release molecular H_2 with a purity higher than 94 wt%. The other possible explanation of the significant improvement of hydrogen purity, in comparison with the pristine $[Al(NH_3)_6][BH_4]_3$, is the presence of the strongly polarizing Li^+ cation [98] which destabilizes $[Al(NH_3)_6]^{3+}$, similar to the activation made by Mg^{2+} [59].

Interestingly, the complexes of $[Al(NH_3BH_3)(BH_4)_3]$ and Na $[Al(NH_2BH_3)_4]$ desorb pure hydrogen, even though the $H^{\delta+}/H^{\delta-}$ ratios is far from ideal. Moreover, the decomposition products of $Na[Al(NH_2BH_3)_4]$ exhibit a partial reversibility and $[Al(NH_3BH_3)(BH_4)_3]$ demonstrated an endothermic dehydrogenation, which can also be potentially reversible. These observations point out the importance of the composition of the forming products, which may hold a part of the excessive hydridic or protic hydrogens. The fundamental understanding of the composition and the chemical structure of the decomposition products remains one of the most challenging problems for the characterization of the real mechanisms of de- and re-hydrogenation in chemical hydrides.

One of the possible regeneration scenarios can be similar to the hydrogenation of Al via the formation of alanate and alane complexes with Lewis bases. In particular, the hydrogenation of aluminium is possible in presence of the coordinating solvents, such as THF, dimethylether, dimethylethylamine (DMEA) and trierthylamine (TMA) [99–102].

Conclusions and perspectives

The high polarizing power of Al^{3+} makes it a strong complex-forming agent, and thus it alters significantly the properties of well known hydrides, such as borohydrides, amides, amidoboranes, ammonia borane and ammonia. Effectively, Al^{3+} is a strong Lewis acid, serving as a template for chemical transformations involving light chemical and complex hydrides. Remarkably, aluminium is capable of coordinating both the initial hydrogenated species as well as the dehydrogenation products, enabling in some cases a hydrogen desorption reversibility. Thus, this review aims at drawing attention not to the classical Al–H interactions observed in alanates and alane, but rather to the chemistry of light hydrides templated on aluminium atoms. Nevertheless, the Al–H chemistry shares some features with the chemistry of hydrides coordinated to Al^{3+}: the Al atom coordinates 4 or 6 neighbours (H^- or complex hydride units such as BH_4^- and NH_2^- etc.) and typically forms mononuclear complexes.

Al complexes with B- and N-based hydrides were classified in this review according to the charge of the Al-based complex, as anionic, molecular, cationic or "autoionized", where Al is centering both the cation and the anion. In the series of Al-based amides $M[Al(NH_2)_4]_n$, borohydrides $M[Al(BH_4)_4]$ and amidoboranes $M[Al(NH_2BH_3)_4]$, aluminium forms tetrahedral complex anions. The shape of the $[Al(BH_4)_4]^-$ tetrahedron is found to be slightly flattened, as compared to the nearly ideal tetrahedral $[Al(NH_2)_4]^-$ and $[Al(NH_2BH_3)_4]^-$. The molecules of NH_3, AB and their substituted derivatives, stabilize $Al(BH_4)_3$ in a molecular and in cationic forms. Addition of one ligand yields molecular complexes; the coordination of Al in the molecular $[Al(NH_3)(BH_4)_3]$, $[Al(NH_3BH_3)(BH_4)_3]$ and $[Al(CH_3NH_2BH_3)(BH_4)_3]$ resembles the tetrahedral coordination of Al in $[Al(BH_4)_4]^-$. Larger amounts of donor nitrogen ligands displace the borohydride groups from the coordination sphere of Al, creating cation complexes, as, for example, those based on $[Al(NH_3)_6]^{3+}$ cation having the octahedral geometry.

Upon thermal decomposition, the anionic and cationic Al-based complexes evolve different gas products besides hydrogen. Different factors influencing the stability of the complexes and the hydrogen purity were analyzed in the Section Composition-structure-property relations. They include the simultaneous presence of the protic $H^{\delta+}$ and the hydridic $H^{\delta-}$ hydrogens, their atomic ratio, the presence and the lengths of the dihydrogen bonds, but above all the composition of the dehydrogenation products. The latter can retain the excess of hydridic or protic hydrogens, and most importantly favor the reversibility. In particular, we pointed out that the presence of both boron and nitrogen atoms allows the formation of unique decomposition products prone to rehydrogenation.

An excellent example where Al^{3+} serves as a template for the conversion of the B- and N-based hydrides is the complex of aluminium borohydride with ammonia borane, $[Al(NH_3BH_3)(BH_4)_3]$ [25]. The endothermic release of two equivalents of hydrogen leads to the formation of $[Al(NHBH)(BH_4)_3]_n$, where the dehydrogenated ammonia borane remains coordinated to the Al atom. This encourages a search for other Al-based Lewis acids, less challenging with respect to stability and safety than aluminium borohydride. A substitution on the coordinated AB should prevent further dehydrogenation of the intermediate, and permit a thorough exploration of their reversibility. Therefore, the family of $[Al(RNH_2BH_3)X_3]$ (X = anion) should be investigated in detail.

The thermal decomposition behavior in $M[Al(NH_2)_4]_n$ and $M[Al(BH_4)_4]$ anionic complexes is quite different from each other. In particular, the decomposition temperatures for M $[Al(NH_2)_4]_n$ series increases with the electronegativity of M, while the opposite trend is observed for the borohydrides M $[Al(BH_4)_4]$. Both systems contain an excess of either protic or hydridic hydrogens, which creates a significant amount of NH_3 and B_2H_6 or even $Al(BH_4)_3$ upon the thermal decomposition. Anionic $M[Al(NH_2)_4]_n$ and $M[Al(BH_4)_4]$ potentially might be combined in RHCs with other hydrides containing the counter-charged hydrogens. In particular, the interaction between $M[Al(NH_2)_4]_n$ and $M[Al(BH_4)_4]$ is interesting, since the ability of Al^{3+} to coordinate both nitrogen or boron can be the good basis for the reversibility of the decomposition products. The family of $M[Al(NH_2BH_3)_4]$ is another interesting partly reversible system with high hydrogen content, with a potential for combining in RHCs with other hydrides.

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